The Distribution and Chemical Constituents of the Farinose Exudates in Gymnogrammoid Ferns

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Many members of the Polypodiaceae *sensu lato* show a conspicuous, yellow or white deposit on the lower surface of their fronds. Therefore, they are often called gold ferns, gold-back ferns, silver ferns, or silver-back ferns. This is especially true for members of the genus *Pityrogramma* Link. Such deposits also occur in *Cheilanthes* Swartz and *Notholaena* R. Br., although they are less known because species of these genera are not easily cultivated in greenhouses. The culture of the decorative species of *Pityrogramma* was especially in fashion at the beginning of the 19th century. Both *P. calomelanos* (L.) Link and *P. chrysophylla* (Swartz) Link were grown at Kew beginning in 1790. Fanciers were attracted by the great variability of species and strains and by the formation of various forms and hybrids that occurred during the culture of "*Gymnogramma*." However, the proliferation of hybrids and horticultural forms led to serious taxonomic confusion. Domin's (1929) statement is still valid: one can easily find completely different species or hybrids grown in greenhouses under the same name. Even recently in botanical gardens the name *P. sulphurea* (Swartz) Maxon has been applied to varieties of *P. chrysophylla* and *P. austroamericana* Domin.

ANATOMICAL OBSERVATIONS

The special anatomical features of the gymnogrammoid ferns were described rather early. Schkuhr (1804, p. 4, *t. 4*) reported that the lower surface of the fronds of the Schwefelgelber Vollfarn, now *Adiantum poiretii* var. *sulphureum* (Kaulf.) Tryon, were covered with an amorphous, yellow web. We owe to Schkuhr charming drawings of entire plants. As to my knowledge, the first detailed figures showing stalked glands themselves were published by Link (1842, *t. III, figs. 7-9*). De Bary (1877, p. 105) gave a good description of farina-dusted capitate hairs, or "pili pulverulenti" as he called them. The farinose coating of these plants is not excreted by the entire epidermis, like a true wax coating, but is formed exclusively by the globose terminal cell of small hairs which have a short, unicellular stalk. The wax is exuded on the whole surface of the terminal cells in the shape of rod- or needle-like crystals. Weatherby (1920) also has clearly described the glands and farina of *Pityrogramma triangularis* (Kaulf.) Maxon. A description similar to that of De Bary (1877, p. 105) was given by Nayar (1962) for *Cheilanthes:* "This large terminal cell secretes the waxy substance which appears like minute rods which are radially placed around the cell. On older stipes the hairs wither and the rods break up to form a powdery mass." De Bary (1877, p. 105) also published a drawing of such a capitate gland which is so far unsurpassed, showing the excreted material (*Fig. 1*). This figure has been copied by many authors, including Blasdale (1893). Comparatively less clear is the drawing by Höhlke (1902), which

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was copied even by Ogura (1972, p. 130). Höhlke stated that the cuticle was not lifted by the formation of secretions. He asserted that the exudate was formed in the "cell membrane" (i.e., cell wall) and he believed he saw pores in which the cuticle had been penetrated by the rods of exudate. Further drawings were published by Molisch (1923, p. 128), Bower (1923, p. 186), Dous (1927), and Nayar (1964). A small microphotograph was published by Smith et al. (1971). It should be noted here that epidermal waxes may form very similar filaments, as shown for example by Gunning and Steer (1977, *t. 9a, b*).

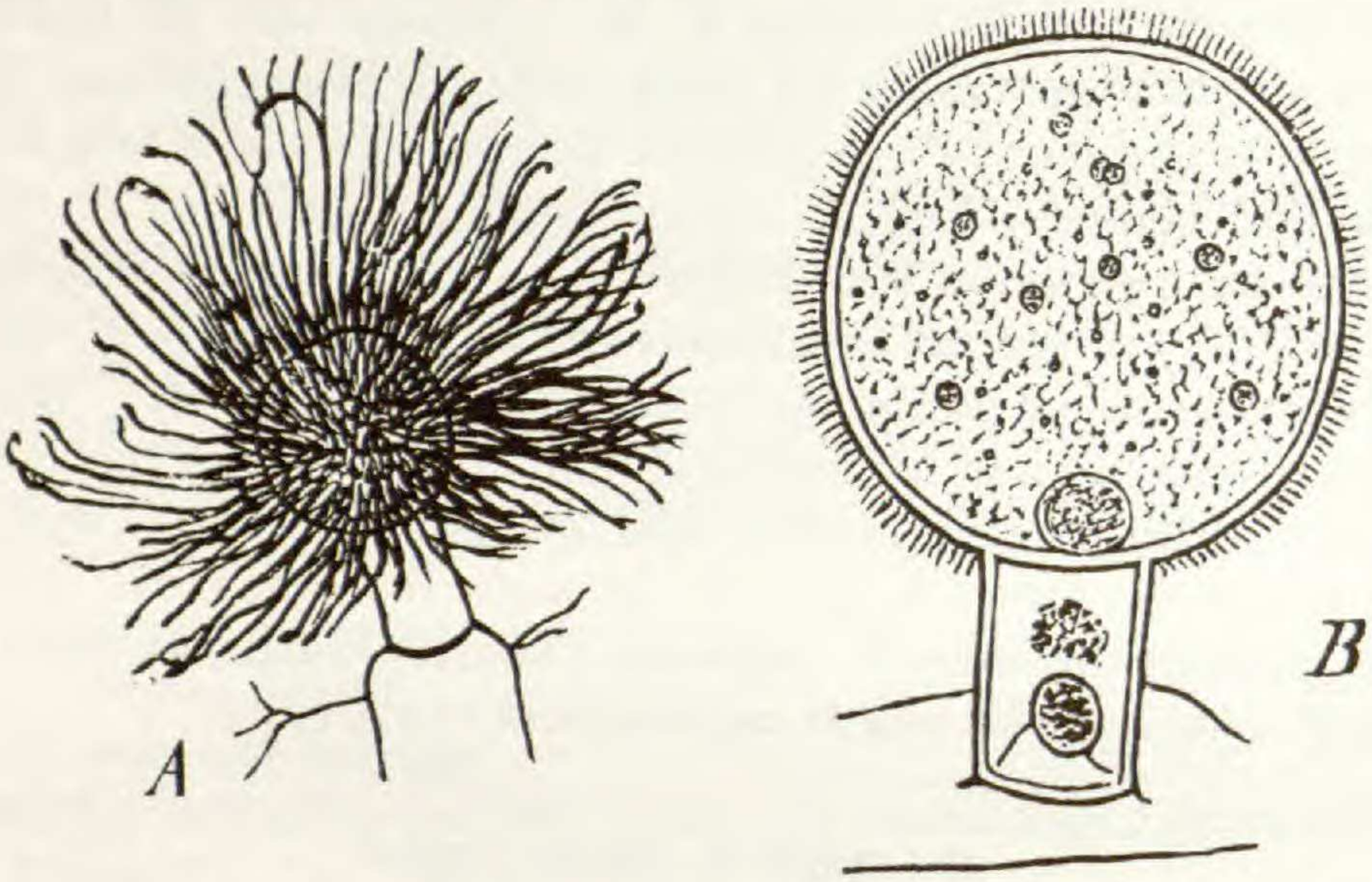

FIG. 1. Pili pulverulenti of *Pityrogramma tartarea* (B rinsed with alcohol), after De Bary (1877).

There has been only one investigation of the ultrastructure of exudate-secreting glands. Schnepf and Klasova (1973) studied the glands of *Pityrogramma chrysoconia* (Desv.) Maxon by transmission electron microscopy. They belong to the group of glands with a tubular, smooth endoplasmic reticulum as the dominant cell component; this means they are similar to those excreting volatile oils. The plastids seem to be involved in the formation of the flavonoids, but there is no proof of their accumulation in the vacuole. The flavonoids penetrate the cuticle and crystallize on its surface. These results resemble those obtained from the glands of *Primula* by Wollenweber and Schnepf (1970), which are likewise regarded as merocrinic glands by Lüttge and Schnepf (1976). The value of the single investigation by scanning electron microscopy (Guervin et al., 1971, on *Gymnogramma sulphurea* Desv.) is diminished because the authors illustrate and discuss the structure of a "cupula," which obviously is an artifact caused by shrinking of the capitate cell during fixation.

The location of the secretory glands varies. Farinose coatings usually are developed on the lower surface of fronds, but in some species they may appear, although less pronounced, on the upper surface, as in *Notholaena aliena* Maxon, *N. grayi* Davenp., *N. leonina* Maxon, *N. rosei* Maxon, *N. schaffneri* (Fourn.) Underw., and some others, according to Tryon (1956). Sometimes farina on the upper surface appears only in dots produced by isolated glands, as can be ob-

served on young fronds of *Pityrogramma austroamericana (Fig. 2).* Occasionally farina is produced abundantly on the rachis, mainly at its base, as in *Cheilanthes farinosa* (Forsk.) Kaulf., *P. calomelanos,* and *P. chrysophylla.* Blasdale (1877) stated, "Though normally occuring on the lower surface only they may appear on the upper, and in all cases they are distributed quite uniformly, that is, without reference to the sori, veinlets or other organs." However, in some species only the fertile pinnules have farinose coatings, as in *Onychium siliculosum* (Desv.) C. Chr. In *Pityrogramma trifoliata* (L.) Tryon, very young fronds bear sporadic patches of farina that soon disappear, and the fertile pinnae also have a farinose coating. In *P. calomelanos* I observed glands on the primary fronds, and according to Bower (1923, p. 199), they appear on the prothallia of *Notholaena trichomanoides* (L.) Desv.

Commonly either hairs and scales or a farinose coating—but not both—occur on the laminae of a single species, but exceptions are found in *Notholaena.*

In *N. aschenborniana* Klotzsch and *N. galeottii* Fée, the wax-like indument can be completely covered by scales. On the other hand, in *Cheilanthes* the separation into genera of the two sections *Cheilanthes* and *Aleuritopteris* Fée, as supported by some authors, is possible only because the two indument types exclude each other.

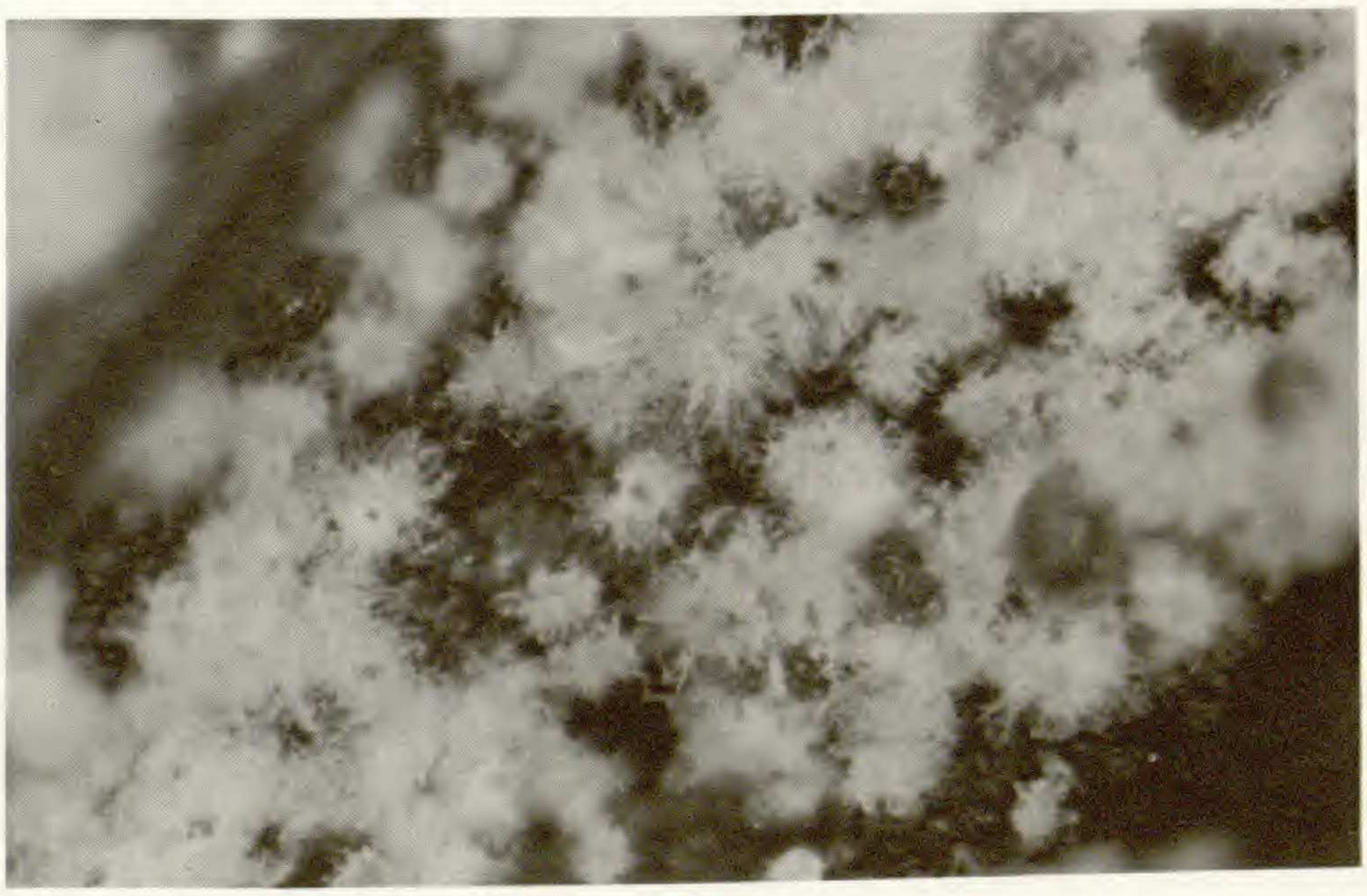

FIG. 2. Farina glands on a young frond of *Pityrogramma austroamericana.*

CHEMICAL NATURE OF EXUDATES

De Bary (1877, p. 105) was probably the first to distinguish farinose coatings ("mehlige Überzüge") from wax coatings. However, the material excreted by gymnogrammoid ferns was usually regarded as a wax-like substance up to the middle of the last century. In 1844, Göppert called it a resin, according to Wiesner (1876, p. 236). Klotzsch (1851) introduced the term "pseudo-stearoptenes" for a chemically undefined group of compounds he characterized as "parts of volatile

oils and resins condensed by heat withdrawal." He assumed that these compounds contain oxygen and counted among them coumarin from *Melilotus officinalis* and "Primula camphor" from *Primula auricula*. Wollenweber (1974) has shown the latter to be a mixture of various flavones, and therefore Klotzsch came rather close to the truth. On the other hand, he erroneously stated that excretion of the dry, farinose mass of fern fronds occurs without glands. Wiesner (1876) called the coatings of ferns "crystalline efflorescences," which he distinguished from plant waxes. The chemical classification of the substances, which were not precisely defined at that time, followed their solubility in water, alcohol, ether, and other solvents. From such investigations, Göppert derived his opinion that the yellow coatings of what is now called *Pityrogramma chrysophylla* are related to resins. This opinion was also expressed by Höhlke (1902). Christ (1897) used the terms "wax flour," "wax powder," or "farina" ("Mehl"), whereas Strasburger (1905, p. 87) called the exudate a "greasy substance." Haberlandt (1918, p. 477) mentioned the capitate hairs of *Gymnogramma* in a chapter dealing with oil, resin, slime, and gum glands. Möbius (1927, p. 152) compared the farinose coatings with wax exudates, Wetzel in Verdoorn (1938, p. 360) classified them with volatile oils as "resinous substances," and even Ogura (1972, p. 126) mentioned "fatty or resinous excretions."

Under these circumstances, it is understandable that taxonomists even at the present time speak of "ceraceous ferns" and of "wax" in keys and descriptions. Apparently the results of recent chemical investigations published in chemical journals have not reached the taxonomists! Even in a phytochemical review by Berti and Bottari (1968, p. 643), the term "wax coatings" was used, despite the more detailed chemical characterization available. This discrepancy has been mentioned several times in the literature (e.g., Smith et al., 1971).

According to strict chemical definition, waxes are esters of long-chain fatty acids with long-chain primary monovalent alcohols, in contrast to fats and oils, which are composed of glycerol esters. According to botanical terminology, waxes are less strictly defined, and include other fatty acid esters, paraffins, primary and secondary alcohols, ketones, and free n-fatty acids (Kreger, 1958). Such substances may produce bluish-white hues on the surface of some ferns, but do not form the farina of the Gold and Silver Ferns, although some paraffins may be present as occasional minor components. I recommend the use of the neutral terms "farina" and "farinose" in describing these coatings, both in ferns and in primulas, for these terms do not interfere with chemical definitions. These terms already have been used by some authors (e.g., Knobloch, 1976).

CHEMICAL INVESTIGATIONS OF FLAVONOIDS

Pityrogramma.—The first chemical analysis of the farina in *Pityrogramma* was carried out by Blasdale (1893, 1903) on *P. triangularis* (Kaulf.) Maxon. He isolated an ether-soluble, yellow substance which he called "ceroptene," and which he recognized as a benzene derivative, although he did not know its molecular structure. Using modern methods like ultraviolet, infrared, and mass spectros-

copy, Nilsson (1959) established the structural formula for ceroptin as that of a chalcone-like substance (*Fig. 3*, compound *1*).[1] Zopf (1906) isolated a red substance from *P. chrysophylla and "P sulphurea"*[2] which he called "gymnogrammene" and from *P. calomelanos* a white substance he called "calomelanene." He observed that the color of gymnogrammene depended on the shape and size of the

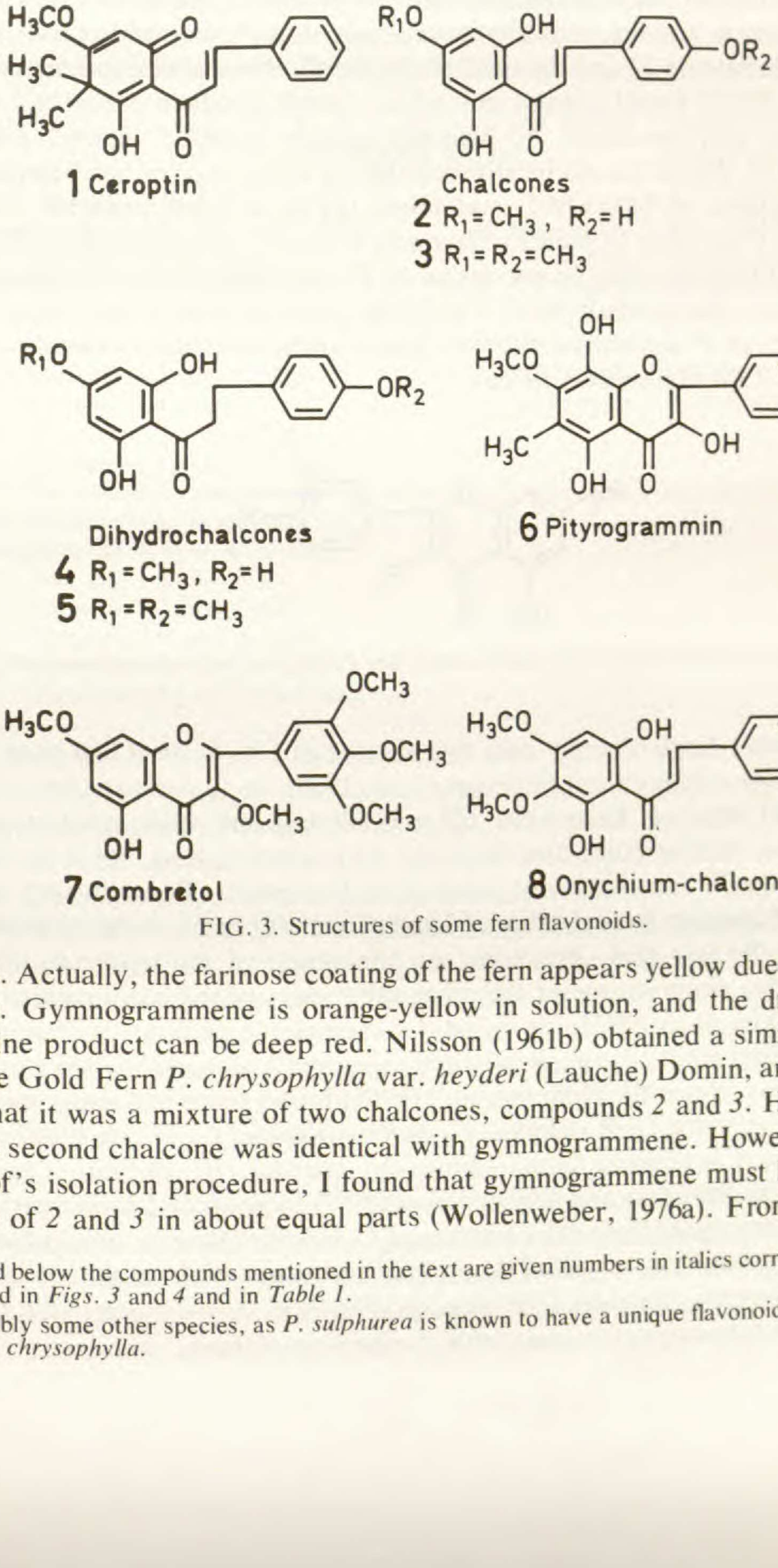

FIG. 3. Structures of some fern flavonoids.

crystals. Actually, the farinose coating of the fern appears yellow due to the small crystals. Gymnogrammene is orange-yellow in solution, and the dry, coarsely crystalline product can be deep red. Nilsson (1961b) obtained a similar material from the Gold Fern *P. chrysophylla* var. *heyderi* (Lauche) Domin, and he recognized that it was a mixture of two chalcones, compounds *2* and *3*. He supposed that the second chalcone was identical with gymnogrammene. However, repeating Zopf's isolation procedure, I found that gymnogrammene must have been a mixture of *2* and *3* in about equal parts (Wollenweber, 1976a). From the Silver

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[1]Here and below the compounds mentioned in the text are given numbers in italics corresponding with those used in *Figs. 3* and *4* and in *Table 1*.

[2]Presumably some other species, as *P. sulphurea* is known to have a unique flavonoid pattern unlike that of *P. chrysophylla*.

Fern *P. chrysophylla* var. *marginata* Domin, Nilsson (1961a) isolated and identified a mixture of the corresponding dihydrochalcones *4* and *5*. Compound *5* is presumably identical with Zopf's calomelanene (Wollenweber, 1976a). The yellow form of *P. calomelanos* was investigated by Bohm (1968), who by indirect evidence recognized chalcone *3* as the main component of the farina. Star and Mabry (1971) found the dihydrochalcone *5* as the major component in the white form of the same species, but dihydrochalcone *4* in *P. tartarea* (Cav.) Maxon, together with flavone *27* and flavonol *14*. In the *P. triangularis* species complex, Smith et al. (1971) found chemotypes which mainly produce ceroptin *1* and the new flavone pityrogrammin *6*, whereas others produce methyl ethers of kaempferol (*15*, *18*). It should be stressed that no other species has been found in the investigations of Star (1977) and Dietz (1978) to form ceroptin. From *P. chrysoconia* I was able to identify flavonols *9* and *11* (Wollenweber, 1972), and later I found that the light yellow farina of *P. austroamericana* is composed of chalcone *3* and dihydrochalcone *5*. The thick, white coating on the under surface of the fronds of *P. lehmannii* Hieron. from Colombia consists mainly of dihydrochalcone *5* (Wollenweber, 1976a).

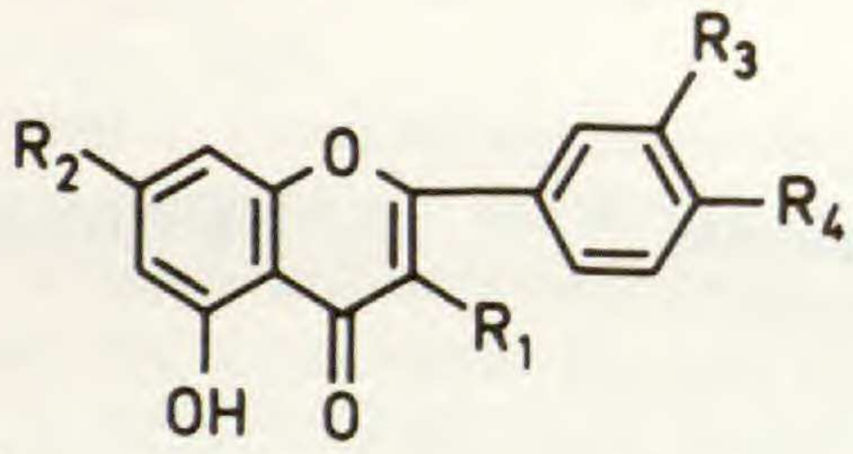

FIG. 4. General structure of flavonols and flavones. See *Table 1* for the chemical structures of groups R_1 through R_4.

Cheilanthes.—Until recently only two species of *Cheilanthes* had been investigated for farina composition. Erdtman et. al (1966), in *C. farinosa* from Taiwan, found methyl ethers of kaempferol (*18* and *19)* and one other substance which, based on the melting point and from our own observations, must be apigenin dimethyl ether *29*. In addition to these three flavonoids, Rangaswamy and Iyer (1969) found another methyl ether of kaempferol *(16)* in *C. farinosa* from South India. It is obvious that, depending on the origin of the material, additional flavonoids may occur or one or the other substances of the basic pattern may be missing. Sunder et al. (1974) identified the kaempferol derivatives *16* and *19* and apigenin methyl ether *27* in *C. longissima* (apparently an unpublished name) from the Himalayas. Recently Wollenweber (1976b) found these and other substances in *C. albomarginata* C. B. Clarke, *C. bullosa* Kunze, *C. grisea* Blanf., and *C. rufa* D. Don. *Cheilanthes kuhnii* Milde var. *brandtii* (Fr. & Sav.) Tagawa has been shown by Serizawa and Wollenweber (1977) to produce a farina very similar to that of *C. farinosa*. The sticky exudate of *C. viscida* Davenp. contains apigenin and its methyl derivatives (*26-29*), probably together with terpenoid materials. Additional species are under investigation. *Figure 4* shows the general structure of all known fern aglycones and *Table 1* enumerates them.

Notholaena.—Prior to the report of Wollenweber (1976b), no flavonoid data were published for *Notholaena*. This report contained results from individual specimens of *N. candida* (Mart. & Gal.) Hooker var. *candida, N. schaffneri* (Fourn.) Underw. var. *nealleyi* (Seaton) Weath., and *N. standleyi* Maxon. These species also produced some compounds which occur in *Cheilanthes*, and *N. candida* var. *candida* excretes a very rare pentamethyl ether of myricetin, combretol *7*. Results for many more species, mostly from several specimens each, recently were published by Wollenweber (1977a, b).

TABLE 1. FLAVONOLS AND FLAVONES FOUND AS COMPONENTS OF FERN FARINA.

Flavonols (R_1 = OH)

9 Galangin (R_2 = OH, R_3 = R_4 = H)
- *10* Galangin-3-methyl ether
- *11* Galangin-7-methyl ether

12 Kaempferol (R_2 = R_4 = OH, R_3 = H)
- *13* Kaempferol-3-methyl ether
- *14* Kaempferol-7-methyl ether
- *15* Kaempferol-4'-methyl ether
- *16* Kaempferol-3,7-methyl ether
- *17* Kaempferol-3,4'-methyl ether
- *18* Kaempferol-7,4'-methyl ether
- *19* Kaempferol-3,7,4'-methyl ether

20 Quercetin (R_2 = R_3 = R_4 = OH)
- *21* Quercetin-3-methyl ether
- *22* Quercetin-3,7-methyl ether
- *23* Quercetin-7,3'-methyl ether
- *24* Quercetin-3,7,4'-methyl ether
- *25* Quercetin-3,7,3',4'-methyl ether

Flavones (R_1 = OH)

26 Apigenin (R_2 = R_4 = OH; R_3 = H)
- *27* Apigenin-7-methyl ether
- *28* Apigenin-4'-methyl ether
- *29* Apigenin-7,4'-methyl ether

30 Luteolin (R_2 = R_3 = R_4 = OH)
- *31* Luteolin-7-methyl ether
- *32* Luteolin-3'-methyl ether

Other genera.—There are a few species of other genera which exhibit farinose excretions. One is *Onychium siliculosum*, which produces a mixture of chalcone *2* and the new chalcone *8* (Ramakrishnan et al., 1974, as *O. auratum)*. A second is *Adiantum poiretii* var. *sulphureum (A. sulphureum* Kaulf.) which, in addition to chalcone *2*, exudes dihydrochalcone *4* and traces of flavonols *9* and *11* (Wollenweber, 1976b). *Negripteris scioana* (Chiov.) Pic. Ser. and *Sinopteris albofusca* (Baker) Ching also show a farinose deposit on the lower surface of their fronds; they are under investigation now. Lellinger (1967) reported that some species of *Pterozonium* have a yellow, orange, or reddish farina. This seems to consist of chalcones, for I have identified chalcone *3* in one specimen of *P. brevifrons* (A. C. Smith) Lellinger.

It is striking that the components of fern farina are almost exclusively methyl derivatives of flavonoids, and so are rather non-polar compounds, for flavonoids usually occur as glycosides dissolved in cell sap. Excretions on the winter buds of certain trees, e.g., *Populus* (Wollenweber, 1975a) and Betulaceae (Wollenweber, 1975b), also contain methylated flavonoid aglycones. There the necessity for lipophilic properties is more evident because these excretions are often formed by remarkable amounts of lipids (volatile oils, terpenoids, phytosterols, and fats),

and the flavonoids are dissolved in this material. The farina of *Primula* also consists almost exclusively of a pure mixture of non-polar flavonoids (Wollenweber, 1974). Excretions of secondary plant products usually are lipophilic (Lüttge & Schnepf, 1976, p. 266). It may be assumed that this peculiarity correlates with the excretion mechanism, which is almost completely unknown.

Considerable amounts of material can be excreted by farinose ferns. In *P. austroamericana,* we obtained 480 mg of flavonoids from 54 g of air-dried fronds; in *P. calomelanos,* 32 g from 1 kg; in *N. candida* var. *copelandii* (C. C. Hall) Tryon, 0.78 g from 26.2 g; and in *P. lehmannii,* which produces farina abundantly, 9.1 g from 165 g. These are amounts of 0.9-5.% of the dry weight of the fronds.

CHEMICAL INVESTIGATIONS OF OTHER COMPOUNDS

In a few exceptional cases, white farina on ferns can be due to quite different lipophilic materials. In *Cheilanthes argentea* (Gmel.) Kunze, we isolated a major component that possibly is a phytosterol; the analysis has not yet been done. *Lophosoria quadripinnata* (Gmel.) C. Chr. (Cyatheaceae), which appears glaucous rather than farinose, has a weak deposit probably consisting of a mixture of triterpenes. This material also is under investigation. The n-alkanes, which lead to the glaucous appearance of such polypodiaceous ferns as *Phlebodium aureum* (L.) J. Smith, have also been found as minor components in *Pityrogramma austroamericana* and *P. lehmannii.*

Some publications have reported the occurrence of hydrocarbons, long-chain aliphatic alcohols, fatty acids, and terpenoids in ferns. Long-chain alkanes are widely distributed; among them those with odd-numbered carbon chains (C_{25}-C_{35}) predominate. Long-chain aliphatic alcohols are found in wax esters; pentacyclic triterpenes of the hopan series are abundant in the group of isoprenoids; among the phytosterols, sitosterol is dominant (Bottari et al., 1972; Seigler et al., 1975; Jamieson & Reid, 1975; Lyttle et al., 1976). Unfortunately, it is not obvious from the cited papers whether the substances are internal components of the plants or whether they are deposited externally. The same is true for the sesterpenes (Kahn et al., 1969; Iyer et al., 1972, 1973) and the ecdyson analogues (Imai et al., 1969; Faux et al., 1970). When an extract of ground material is made, it can not be seen where the extracted substances were located. Even in some clearly farinose species like *Cheilanthes farinosa* and *Onychium siliculosum,* where whole plants have been ground and extracted only people familiar with the plants realize that the flavonoids described are of external origin. When chemical work of this kind is done, more attention should be paid to the location of the chemicals being analyzed.

FLAVONOID STRUCTURES AND FARINA COLOR

Chalcones are responsible for intense yellow coloration in most cases. The decorative Gold-back Fern *P. chrysophylla,* for example, owes its bright yellow color to chalcones *2* and *3*. The less intense yellow of *P. austroamericana* is due to a mixture of chalcone *3* with dihydrochalcone *5*. The same hue in *Adiantum sulphureum* is produced by chalcone *2* and dihydrochalcone *4*. The strong colora-

tion of *Onychium siliculosum* is due to the presence of chalcones *2* and *6*. We observed that the ratio of chalcone *2* to *6* influences the deepness of the hue. Such relationships of colors with ratios of compounds is found especially with mixtures of chalcones and dihydrochalcones, but also occurs to a lesser extent in mixtures of flavones and flavonols. The intense orange of *C. mossambicensis* Schelpe and *C. welwitschii* Hooker ex Baker is accounted for by chalcone *2*, as shown by Wollenweber (1977b).

In *Cheilanthes* and *Notholaena*, white, whitish, and weakly yellow farina dominate (except for some chalcone-colored species and varieties cited below), due to the presence of flavones and flavonols. But it is more difficult to recognize relationships between composition and farina color. In species which produce derivatives of apigenin, like flavones *26-28* in *Notholaena grayi* and *26-29* in *N. greggii* (Kuhn) Maxon, the farina is white. Pure white farinas are also encountered in *N. candida* var. *candida* (caused by two methyl ethers of myricetin, *7* and an as yet unknown tetramethyl ether) and in *N. candida* var. *copelandii* (caused by galangin (*9*) and the 3-monomethyl ethers of galangin, kaempferol and quercetin (*10*, *13*, and *21*). The white form of *N. californica* D. C. Eaton produces derivatives of apigenin (*27*) and luteolin (*30* and *31*), kaempferol (*16*), and quercetin (*21*, *22*, and *24*). The light yellow farina of *N. standleyi* consists of derivatives of kaempferol only (*12-17*). *Cheilanthes farinosa* is mostly pure white or whitish, the farina being composed of methyl ethers of apigenin (*29*), kaempferol (*14*, *18*, and *19*), and sometimes quercetin (*23*) as a basic pattern. A faintly yellowish hue may depend on quantitative differences which have not yet been analyzed, but perhaps kaempferol derivative *19* prevails. The white farina of *C. albomarginata* is due to genkwanin (*27*) and to two kaempferol methyl ethers (*14* and *16*); *C. grisea*, also white, in addition produces two kaempferol derivatives (*18* and *19*).

Besides the variation in composition, the density of the deposit and the size of the particles also may play a role in color expression.

THE FUNCTION OF FARINAS

The term secretion, according to the definition of Schnepf (1969), is to be used for exudates produced by organisms or cells as a result of their interaction with the environment, or which are produced as an immediate consequence of such interaction. The term excretion, on the other hand, refers to waste matter, the production of which is not directly related to the environment. Schnepf emphasized that a sharp demarcation of both terms is neither possible nor necessary. Thus the word excretion may well be used when talking about exudates of farinose ferns, although the term secretory glands may also be used as a general term.

Many years ago, Blasdale (1893) considered the possible function of glandular cells on *Pityrogramma* fronds and *Primula* leaves, and he remarked that their existence gave rise to speculation. In his opinion, one could not help recognizing glandular cells as a mechanism for some definite purpose, as he could not regard the material excreted as mere waste products. He found one plausible function: protection of young spores as well as the lower epidermis against "excessive

moisture," since the position and chemical nature of the farinose material keep water off the lower surface of the fronds. He thought a second role was to protect these natives of arid regions against excessive transpiration, since many allied species without glands had a thick growth of hairs or scales. Höhlke (1902) attributed to the "resin" of *Gymnogramma* (i.e., *Pityrogramma*) the function of an insect deterrent "because the plants in the greenhouse are free of destructive insects even in summer." He felt confirmed in his opinion by the observation that the coating was thick on young fronds and diminished or even vanished on old fronds, which no longer needed this protection. This misinterpretation was probably based on incomplete observation; secretory glands stand much further from each other on adult fronds than on juvenile ones because new glands do not develop during the later stages of frond growth and the glands no longer are active. Hence, the excretion material is dispersed. Partly it crumbles as a dry mass, and partly it is rinsed off by rain. Nayar (1964) states, "On mature stipes the glandular hairs shrivel, leaving powdery covering which is often lost on old stipes."

Haberlandt (1918, p. 478) stated that the physiological and ecological importance of the epidermal glands in general depends on the nature of the exudate. Apart from the possibility that in some cases useless end products of metabolism may be secreted, secretions usually have some significance, like protection against strong transpiration or against animal attack. These are the same possible functions that Blasdale and Höhlke attributed to fern glands. Bower (1923, p. 198) was convinced of the role of fern excretions as water repellents. Linsbauer (1930, p. 123) accepted primarily their role in preventing excessive transpiration. However, he regarded speculations on the ecological significance as idle. Nilsson (1959) found it tempting to speculate on the possible physiological significance of the ceroptin coating of *Pityrogramma triangularis,* and he mentioned that the β-triketones (in which he then included ceroptin) are known to exhibit antibacterial and sometimes insecticidal activity. I think some antibacterial effect can certainly be attributed to most phenolics, and this could apply to fern farina in general, but we have no proof as yet. Swain (1973) speculated about quite a different function. He assumed that the chalcones "in the sori" of *P. chrysophylla* might control some light-catalyzed reaction. However, this is quite unlikely since the chalcones are produced by glands of the epidermis. All considerations on the possible functions of fern farina may be summarized by the comment of Harborne et al. (1975, p. x) on flavones and flavonols: "The raison-d'être . . . still remains as mystery."

DISTRIBUTION OF FLAVONOIDS IN THE GENERA

All the ferns so far found to excrete flavonoid aglycones belong to the Polypodiaceae subfam. Gymnogrammoideae, and to sects. Cryptogrammeae (*Onychium*), Gymnogrammeae (*Pityrogramma* and *Pterozonium*), Adianteae (*Adiantum*), and Cheilantheae (*Cheilanthes, Negripteris, Notholaena,* and *Sinopteris*), according to the system in Engler's "Syllabus" (Melchior & Werdermann, 1954). Hooker and Baker (1868, p. 384) proposed *Gymnogramma* sect.

Ceropteris (Link) Hooker & Baker for farinose species of *Pityrogramma* and *Notholaena* sect. *Cincinalis* (Desv.) Hooker & Baker (1868, p. 373) for farinose species of *Notholaena*. Farinose *Cheilanthes* species are called *Aleuritopteris* by some authors, or are at least separated as *Cheilanthes* sect. *Aleuritpteris* (Fée) Hooker & Baker, as in Nayar (1962).

The various species of *Pityrogramma* in general produce chalcones and/or dihydrochalcones (*2-5, 8*); flavones and flavonols can occur as minor components. *Cheilanthes* and *Notholaena,* on the other hand, produce flavones and flavonols (*7* and *10-32*). Known exceptions in *Pityrogramma* are *P. triangularis* (Star et al. 1975b) and *P. chrysoconia* (Wollenweber, 1977a). In both cases, only some forms or chemotypes differ from the chalcone-dihydrochalcone scheme. Exceptions in *Cheilanthes* are *C. aurea* Baker, *C. aurantiaca* (Cav.) Moore, *C. chryosophylla* Hooker, *C. mossambicensis,* and *C. welwitschii.* These species excrete chalcones. There is also one form of *C. welwitschii* which produces a dihydrochalcone. In *Notholaena,* I know three species which exude chalcones: *N. aurantiaca* D. C. Eaton, *N. nivea* var. *flava* Hooker, and the yellow form of *N. sulphurea* (Cav.) J. Smith. Dihydrochalcones also may occur, as in *N. lemmonii* D. C. Eaton and the white form of *N. sulphurea*. Thus Bohm's (1975) statement that "*Pityrogramma* is the only fern genus known to accumulate chalcones and dihydrochalcones" is no longer true.

CHEMOTAXONOMIC EVALUATION

Alt and Grant (1960) showed that the varieties of *Pityrogramma triangularis* constitute a polyploid complex which includes diploids, triploids, and tetraploids. Smith et al. (1971) showed that correlations for these taxa exist between spore morphology, cytology, and pigment chemistry. According to the composition of farina, they distinguished four chemotypes: ceroptin type, kaempferol-methyl ether types A and B, and a type with kaempferol derivatives and ceroptin. According to their data, different ploidy levels can not be distinguished by farina analysis. The complexity of chemical and cytological variation allowed two alternative interpretations: either *P. triangularis* is one species existing as an autoploid complex and consisting of genetic variants with the same basic genome, or it is a segmental allopolyploid group with several genomes (cf. Mabry, 1973). Later, more detailed chemical investigations included the analysis of internal flavonoid glycosides (Star et al., 1975a). Diploids and tetraploids can be distinguished by this method within the ceroptin type as well as within one kaempferol methyl ether type. Thus, in *P. triangularis* var. *triangularis* four taxa can be outlined by means of chemical data. The tetraploid kaempferol methyl ether chemotype has a glycoside pattern composed of those of two diploids, and so may be of alloploid origin. The tetraploid ceroptin chemotype, on the other hand, may be of autoploid origin. Finally, n-alkanes occuring in these excretions have been investigated by Seigler et al. (1975). As expected, this class of compounds is not helpful for chemotaxonomic investigation. However, the average percentage of C_{33} lends support to the previous suggestions concerning the origin of tetraploids.

My own investigations as yet have been less far-reaching. Difficulties in obtaining plant materials and the small size of most samples received from herbaria has limited analysis to external flavonoid aglycones. Furthermore, the number of samples received of individual species is still very small. Nevertheless, from the high number of species analyzed, certain trends can be observed.

As stated above, excretions of chalcones and dihydrochalcones dominates in *Pityrogramma*. Apart from the exceptions cited, the occurrence of these substances at present appears to be a genus-specific character. When so far unidentified minor components are included, this suggestion is strongly supported. Thus, an Indian *P. calomelanos* can not be distinguished from a South American *P. dealbata*. On the other hand, in some species, small differences in external flavonoid patterns are noted, the meaning of which is under investigation. The differences probably are not sufficient to consider the plants as different chemotypes. The presumed specificity of farina composition in a few species (Dietz, 1978) still has to be verified.

As far as *Cheilanthes* and *Notholaena* are concerned, it is disappointing that no sharp delimitation of these genera, which are controversial in the taxonomic literature (cf. Knobloch, 1976), is possible by farina analysis. In both genera, methyl ethers of kaempferol, quercetin, and apigenin are synthesized above all others (see *Fig. 4* and *Table 1*). Nevertheless, there are some interesting peculiarities within the genera, even though only a few specimens per species have been analyzed as yet. *Notholaena bryopoda* Maxon (compounds *13, 16, 19*), *N. grayi (26-28)*, and *N. greggii (26-29)* have species-specific flavonoid patterns. Other species show unique patterns, too, but their substances have not yet been identified. *Cheilanthes* also has species/specific flavonoid patterns (Wollenweber, 1976c). The basic patterns may vary slightly by the addition of inconstant compounds. In this infraspecific variation I am inclined to see an expression of variability in biosynthetic capacity, just as we are used to seeing variability in morphological characteristics. Certainly interpretation becomes more difficult when more complicated flavonoid patterns in species like *N. incana* Presl or *N. standleyi* are considered. Infraspecific as well as infra- and inter-populational variation can not be studied from single specimens; extensive field collecting is necessary to accomplish this.

In some cases, variety-specific flavonoid patterns may occur. For example, five specimens of *N. candida* var. *copelandii* are characterized by the 3-methyl ethers of galangin, kaempferol, and quercetin, *10, 13, 21*. Unfortunately, the poly-0-methyl ethers of myricetin (*7* and unknown) are not so constantly encountered in all five specimens of var. *candida*. Nevertheless, evaluated jointly with the additional unknown components, they are typical for this variety and permit inclusion here of three specimens which I received unnamed to variety. Similar examples are known in other *Notholaena* and *Cheilanthes* species.

Chemotypes may exist, e.g., in *N. affinis* (Mett.) Moore and in *N. californica*, where classic taxonomy does not distinguish varieties. Tryon (1965, pp. 47-48) describes the lower lamina surface of *N. affinis* as having "pale yellow to yellow

(rarely white) indument." At present I have six samples of this species, all with light yellow farina. Four show kaempferol (*12*) as the predominant or even sole component; apigenin (*26*) and isokaempferid (*13*) can occur as minor components. Two collections from Costa Rica, however, show unknown compounds instead; the major component of the farina was identified as a flavonol with butyryl side chain (Wollenweber et al., 1978). It is possible to presume the existence of chemotypes, but as yet it is not known whether these are correlated with populations. For *N. californica,* Tryon (1956, p. 74) wrote, ". . . lower [surface] whitish to usually yellow ceraceous." The yellow farina consists of a series of unknown substances now under investigation which show an identical pattern in the eight samples available. But the white farina of three other samples consists of distinct and constant methyl ethers of flavonoids. Here, too, one can presume the existence of chemotypes. It must be left to the taxonomists whether it is justifiable to establish varieties or not. But in both cases both color differences and differences in flavonoid pattern exist.

Tryon (1962, 1964) did not take into account "wax color forms" in ferns in which the color is not correlated with any other characteristic or with geography. For *P. chrysoconia,* he wrote, "Plants with white wax on the leaves and those with yellow wax both occur nearly throughout the range of species and there seems to be no reason to recognize these variants." For *P. chrysophylla,* he wrote, "The white and yellow color forms, although especially striking in this species, do not merit recognition." For *P. calomelanos* and *P. tartarea,* however, he wrote, "In these species the strong correlation of the character with geography seems to provide it with an importance it would otherwise not have." Tyron distinguishes varieties of these species by the farina color (*P. calomelanos* var. *calomelanos,* var. *aureoflava* (Hooker) Weath. ex Bailey, and var. *ochracea* (Presl) Tryon; *P. tartarea* var. *tartarea,* var. *aurata* (Moore) Tryon, and var. *jamesonii* (Baker) Tryon).

Species with very variable patterns of external flavonoids, like *N. schaffneri* in which each sample is different from every other one and no correlation with the established varieties *schaffneri* and *nealleyi* can be detected, are still very puzzling and dictate caution in interpreting flavonoid data In addition, special difficulties are expected with those species in which different colors are observed on a single plant, possibly depending on the age of the frond or plant (Tryon, 1956). These phenomena require further investigation, as do flavonoid studies in general. I would appreciate contributions of fresh material and herbarium specimen fragments (even of widespread species) to support such studies.

My investigations reported here were initiated by Prof. W. Hagemann, of the University of Heidelberg, who first supplied samples of farinose ferns. In view of the rarity of many species and their restriction to tropical regions of the world, the work on this subject would have been impossible without the kind support of many pteridologists. To all of them I am greatly obliged, and I wish to express my gratitude. Thanks are also due to Prof. W. Ullrich, of the Technische Hochschule Darmstadt, for critically revising the manuscript and for his kind help with the English translation.

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